Co-Doping Effect of Nanoscale C and SiC on MgB2 Superconductor

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Co-Doping Effect of Nanoscale C and SiC on MgB_2 Superconductor

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***Abstract*—MgB_2 was thought as a promising superconductor used at temperatures around 20 K for cryogen-free magnet. Nanostructure materials were often selected as MgB_2 additives due to their high chemical reactivity. In this paper, the mixture of nano-C and nano-SiC was doped to MgB_2 bulks and tapes. The co-doping effect of C and SiC on the phase formation, microstructure, and critical current density of MgB_2 bulks and tapes were systematically investigated. The mechanisms for the superconducting properties improvement in co-doped MgB_2 superconductor was analyzed based on the characterization and measuring results.**

***Index Terms*—Co-doping, critical current property, flux pinning, MgB_2.**

I. Introduction

MgB_2 has attractive characteristics for practical application, such as high critical temperature (T_c), 'weak-link free' grain coupling and low material cost. However, the critical current density (J_c) of MgB_2 decreases rapidly under magnetic fields. A number of synthesis techniques have been developed to improve the properties of MgB_2 [1]–[4]. Up to now, the most commonly used procedure is element/compound doping process, as summarized by Bhatia *et al.* [5]. Indeed, many kinds of impurities have been attempted so far. Among these large number of dopants reported, C, SiC, carbon nanotubes, hydrocarbons, etc, are the most promising additives, being effective for enhancement of the irreversibility field (H_{irr}) and J_c in magnetic fields [6]–[9]. It is proved by many experiments that C can be substituted into MgB_2 lattice, and consequently the upper critical field (H_{c2}) and the J_c values in magnetic field will be significantly improved without using expensive raw materials or complicated processing [10], [11].

For MgB_2, the superconductivity originates from the strong electron-phonon coupling in σ bands. So the substitution of boron by carbon would introduce a net of intragranular defects due to crystal lattice distortions and local fluctuations of the superconducting order parameter. Both of them can strongly improve the pinning properties of MgB_2 [12]. At the same time, the carbon substitution has a great impact on the carrier density and impurity scattering [13]. It is expected that carbon, which has one more electron than boron, will donate electrons to the σ band. Also, an increase of impurity scattering within the π band and the modification of band structure can be achieved by carbon substitution. This means a significant enhancement of H_{c2}, and H_{irr} in MgB_2 can be achieved by a controlled carbon substitution.

On the other hand, although the current carrying capacity is not limited by weak links [14], the J_c values of MgB_2 superconductor were obviously affected by the MgB_2 grain connections [15]. In MgB_2 superconductor, the density of the MgB_2 core and the volume of non-superconducting impurities are the main factors that affect grain connections. So the impurities introduced by chemical doping must be considered in discussing the doping effect of different doping materials.

In recent studies [16], [17], co-doping was attempted in MgB_2 to simultaneously enhance both flux pinning and grain linkages, and ultimately to achieve high in-field J_c. On the other hand, it is said that the major enhancement of H_{c2} and J_c for nano-C and SiC doped MgB_2 has a different origin, although both share carbon substitution as an important factor [8]. In this paper, we studied the co-doping effect of nano-C and SiC on the microstructure, magnetic field dependence of J_c and flux pinning for MgB_2 superconductor, and revealed some interesting features which can be correlated with the different superconducting properties.

II. Experimental

Polycrystalline samples of MgB_2 were prepared through an *in situ* reaction process. Powders of magnesium (325 mesh, 99.8%) and amorphous boron (2–5 μm, 99.99%) were weighed out according to the nominal atomic ratio of 1.05: 2. For C (20–30 nm, 98%) and SiC (10–30 nm, 98%) doped samples, the nominal carbon atoms doping ratio is 8 at.% of Mg and B powder. For co-doped samples, the nominal carbon atoms doping ratio for C and SiC are both with 4 at.% of Mg and B powder. The mixtures were milled using a ball mill with agate milling tools for 1 h under air atmosphere. Then the ground powders were unidirectionally pressed into pellet of 14 mm in diameter and ~5 mm in thickness under 10 Mpa pressure. After the pellets were sealed in quartz tubes, they were heat treated at 850 °C for 1 h and then cooled in the furnace to room temperature. For MgB_2 tapes, the fabrication process

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was reported elsewhere [9], while the sintering temperature is 700–900 °C.

The phase identification and crystal structure investigation were carried out using powder x-ray diffraction (XRD). Microstructure and composition analyses were performed using a scanning electron microscopy (SEM). DC magnetization measurements were performed with a superconducting quantum interference device (SQUID) magnetometer.

The magnetization was measured over a wide temperature range between 5 and 20 K in 0–5 T. Bar shaped samples with similar dimensions of about $\mathrm{a} \times \mathrm{b} \times \mathrm{c} = 1 \times 2 \times 3\ \mathrm{mm}^3$ were cut from the sintered pellets. The magnetic J_c was calculated from the height of the magnetization loops $(M - H)$ using a Bean model, where a and b are the dimensions of the sample perpendicular to the direction of applied field, with $\mathrm{a} < \mathrm{b}$. For MgB_2 tapes, the transport I_c at 4.2 K was measured by the four-point-probe resistive method with a criterion of 1 μV cm^{-1}.

III. Results and Discussion

Fig. 1 shows the XRD patterns of the series of *in situ* processed MgB_2 bulks with different doping materials. For the undoped samples, all the diffraction peaks are indicated to be from MgB_2 phase except some peaks of MgO and MgB_4. Besides the impurity phases appeared in undoped samples, Mg_2Si were also found in the XRD patterns of nano-SiC and co-doped samples. It can be seen that the full width at half maximum (FWHM) of the XRD patterns for doped samples is larger than that of undoped samples. This broadening of the FWHM can be explained by the inferior crystallinity and lattice distortion of MgB_2, which usually results in an enhancement of flux pinning strength [18].

Fig. 2 plots the (002) and (110) Bragg reflections of all the samples. Although the accurate lattice parameter can not be obtained from XRD patterns because of the large amount of MgO, it can be seen that the (110) peaks of doped samples are shifted to higher 2θ angle. This indicates that the C substitution for B is actually occurred in doped samples, in accordance with the results of other group [7], [19]. The shift angle of the (110) peak for SiC doped samples is smaller than that of C doped samples. This suggests that substitution of C in the B site by SiC addition is small for sintering temperatures below 1000 °C, compared to samples with C addition, in accordance with Soltanian's work [20]. There was a small shift in the (002) peak for co-doped samples, which maybe due to the problem of loading of sample for the XRD measurement.

The diamagnetic susceptibility data regarding the superconducting transitions for all the samples are shown in Fig. 3. The T_c onset for undoped samples is 38.05 K, while the T_c for SiC doped, co-doped and C doped samples was depressed to 33.67, 33.67, and 33.24 K, respectively. This is in accordance with the shift of (110) peak in XRD pattern, and also consistent with recent results [21]. On the other hand, it can be seen that although the transition line are not the same to each other, the T_c differences is very small for all the doped samples. From this point, we can say that the carbon substitution levels in the doped samples are not different too much.

Fig. 4 shows J_c calculated from magnetization hysteresis loops for the undoped and doped samples. Clearly, the J_c

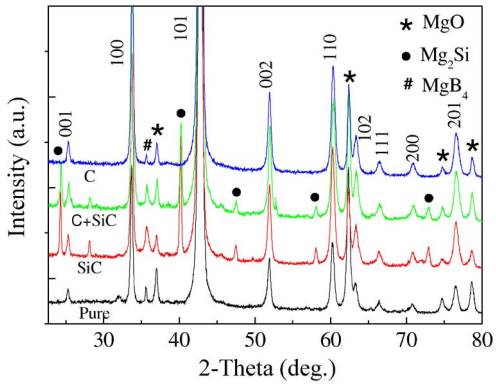

Fig. 1. XRD patterns of doped and undoped bulks sintered at 850 °C. The peaks of MgB_2 indexed, while the peaks of MgO and Mg_2Si are marked by asterisks and circles, respectively.

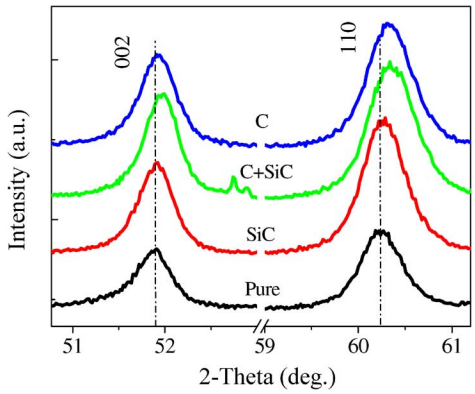

Fig. 2. The (002) and (110) Bragg reflections for doped and undoped MgB_2 bulks sintered at 850 °C.

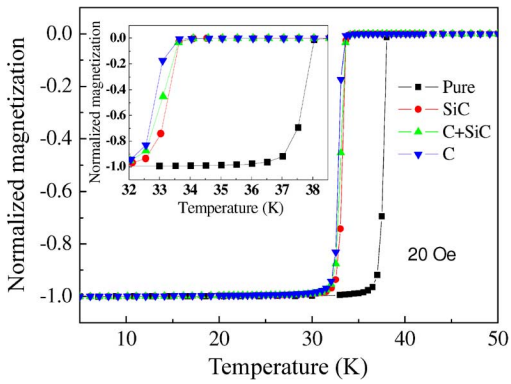

Fig. 3. Temperature dependence of the DC magnetic susceptibility curves of doped and undoped bulks sintered at 850 °C. The curves near the T_c region are enlarged in the inset.

values are improved by doping with all of these materials. For example, compared to undoped samples at 5 K, 4 T, an improvement nearly 3-fold was found in co-doped samples, and a 2-fold improvement was obtained even at 20 K, 4 T. However, the field dependence of J_c have no obviously difference between doped and undoped samples, which maybe due to the low magnetic field measured.

On the other hand, it can be seen that the J_c values have much differences in C, SiC, and co-doped samples. At 5 K, the best J_c value is found in co-doped samples, while the lowest J_c

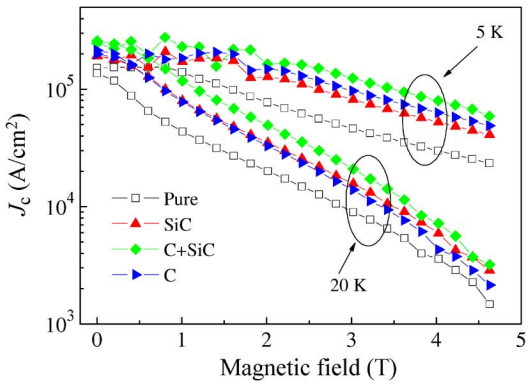

Fig. 4. Magnetic critical current density as a function of the applied magnetic field at 5 K and 20 K for MgB_2 Bulks sintered at 850 °C.

values appeared in SiC doped samples. Considering the reactions happened in SiC doped samples [19], it is proposed that larger amount of impurities existed in MgB_2 core is the main reason. Non-superconducting phases presented in MgB_2 core can enhance the vortex pinning, but also will strongly degrade the connectivity needed for high critical current density if they cluster at grain boundaries [22]. They will strongly decrease the fraction of the cross-sectional area for superconducting current, which was called the active cross section (A_F) by Rowell *et al.* [23]. But for the co-doped samples, this problem seems not so serious, possibly because the impurities are just getting the right balance between act as pinning centers and current obstacle.

Fig. 5 shows the SEM images of all the MgB_2 bulks sintered at 850 °C. MgB_2 particles with hexagonal plate shape are scattered in all of the samples. Compared to undoped samples, there are much larger melted regions in the doped ones, resulting in a better connectivity between MgB_2 grains. Seen from the SEM images, the grain size in doped samples is not so obviously decreased compared to the results of other groups [6], [19]. But it can be imagined that there are larger amount of grain boundaries in doped samples, due to the impurities introduced. These grain boundaries are likely to act as effective pinning centers.

As the superconducting properties of MgB_2 are significantly affected by sintering temperature, so further investigation on the co-doped samples sintered at different temperature will be helpful in the explanation of intrinsic mechanism. Fig. 6 shows the co-doped MgB_2 tapes sintered at different temperatures. For samples sintered at 800 °C, at 4.2 K, J_c reached 2.4×10^4 A/cm^2 and 4×10^3 A/cm^2 at 9 T and 14 T, respectively. The flux pinning was lowered when samples was heated at higher temperature, due to the decreases of grain boundaries caused by the MgB_2 grain growth. This is different to nano-C and SiC doped samples sintered at different temperatures [24], [25].

Nano-C and SiC as MgB_2 doping materials were study hotly these days. H_{c2} and flux pinning of MgB_2 can be significantly enhanced by doping with them. The lattice defects caused by the substitution of B by C, and the inclusion of the coherence-length scale impurities are believed to be the main reasons. The lower

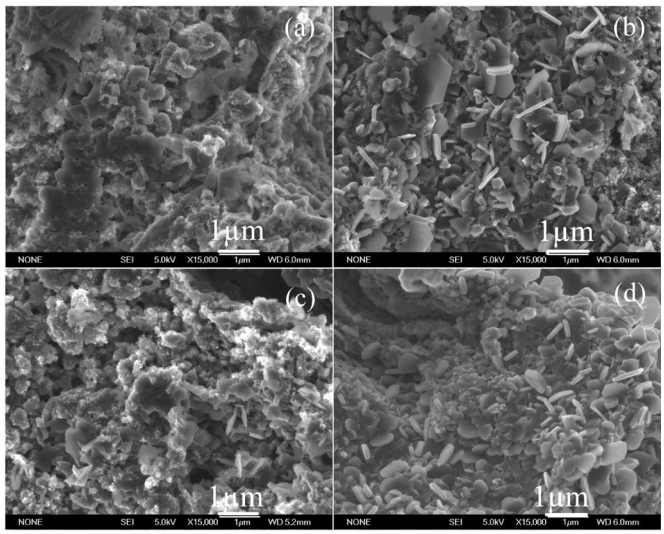

Fig. 5. SEM images of (a) undoped, (b) SiC doped, (c) co-doped, and (d) C doped MgB_2 bulks.

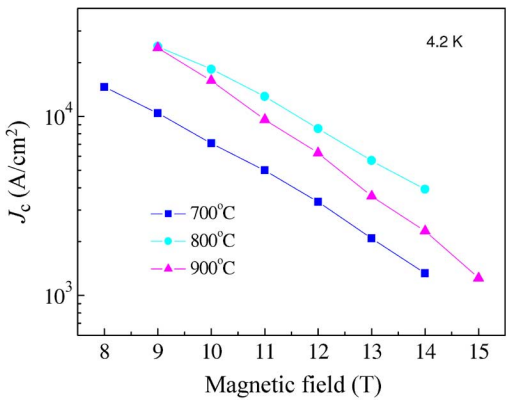

Fig. 6. Transport critical current density as a function of the applied magnetic field at 4.2 K for co-doped MgB_2 tapes.

J_c values in SiC doped MgB_2 bulks may be caused the high sintering temperature [20], but the reason why the co-doped samples have the highest J_c value is still not clear. It seems that the pinning ability can be more significantly enhanced in SiC doped samples, while the grain connection is not seriously damaged in C doped samples. Co-doped samples get the preferable properties of C and SiC doping, and obtained the best J_c values in the measured magnetic fields. Notably, the shift of (110) peak and the decrease in T_c indicated that a certain number of carbon atoms have substituted for boron atoms in MgB_2 core, and the carbon substitution is more pronounced in C doped samples. For the co-doped samples, the best $J_c - B$ property is obtained in samples sintered at 800 °C, show a different mechanism to nano-C and SiC doping.

IV. Conclusion

In summary, we investigated the co-doping effect of nano-C and nano-SiC on the microstructure and superconducting properties of MgB_2 superconductor. It is found that co-doped samples have the best J_c values, because of the enhancement of grain linkages and improvement of H_{c2}. The large amount of

grain boundaries and the substitution of C to B played an important role for the J_c improvement. Different to C and SiC doping, the best J_c was obtained at samples sintered at 800 °C.

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